Structural stability of Cr-related defect complex in diamond for single photon sources: A first-principles study

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We performed first-principles calculations to characterize the structure and electronic properties of Cr-related centers in diamond when oxygen or nitrogen is involved. We found that Cr$_2$V-N$_C$ center with C$_s$ symmetry is energetically favored under N-rich condition, with respect to Cr$_{inn}$, Cr$_{TC}$, Cr$_{2V}$, and Cr$_{2V}$-O$_C$. In analogy to the Cr$_{2V}$ defect, Cr$_{2V}$-N$_C$ center also introduces strongly spin polarized impurity levels into the diamond band, in favor of single-photon emission. The yield of optically active centers of the single photon emitters could be improved by incorporation of N, since the formation energy of Cr$_{2V}$-N$_C$ complex is lower than that of Cr$_{2V}$ under N rich condition. Meanwhile, our calculations indicated that the additional incorporation of O to Cr or (Cr, N) defects introduces not well-separated impurity levels, which will broaden the emission lines.

I. INTRODUCTION

Diamond has been received intensive attention due to the exploration of color centers (nitrogen vacancy (NV) center, for example), which can be used as a single photon emitter, and for quantum computing and quantum communications. Out of more than 500 color centers, less than ten have been identified as bright, stable single-photon emitters so far. The well studied NV centers showed the most possible application in single photon source (SPS) based on its availability of optical readout of the individual electronic spin state. NV centers, however, have a significant drawback of a strong phonon coupling, resulting in a weak zero-phonon line in the emission of single photons. To overcome the limitations of the NV center, alternative color centers, such as silicon vacancy (Si-V center) and nickel related complex (NE8), have been investigated and showed narrow emission lines in the near infrared (NIR). The Si-V centers, however, showed very low emission rates and a very high nonradiative decay term. Both the Si-V and NE8 centers are difficult to fabricate controllably at the single center level.

More recently, a new class of single photon emitters associated with chromium impurities in diamond was discovered following the earlier reported chromium-related centers using optical techniques. The new class of chromium-related emitters showed remarkable properties: narrow luminescence in the NIR region, ultra-bright single-photon emission with the brightest emitter reaching rates of $3.2 \times 10^6$ counts s$^{-1}$, short excited state lifetime $\sim 1-4$ ns, and fully polarized excitation and emission behaviour. However, the atomic structure of the single photon center has not been confirmed. It was suggested by Benecha and Lombardi that it could be a chromium atom in the center of divacancy, while Aharonovich et al. proposed a Cr-X or X-Cr-Y type non-centrosymmetric atomic configuration based on the experimental observations, where X and Y are likely to be oxygen(or sulphur), nitrogen, or vacancy. Aharonovich et al. also observed that the yield of optically active centers of the single photon emitters is obvious with proper concentration of nitrogen, and can be increased by at least one order of magnitude when co-implanted with oxygen (or alternatively sulphur). Previous work suggested that this could be ascribed to the deep donor levels introduced by O or S in the diamond band gap.

In order to understand the microscopic structure of the Cr-related center and investigate the role of nitrogen and oxygen in the formation of the optical centers, we performed first-principles calculations on the configurations of single chromium defect, the defect complexes of (Cr, O), (Cr, N) and (Cr, N, O). First-principles calculations have been successfully helped confirming the micro atomic structures and electronic properties of various color centers in diamond. Here, we found a strong spin orbital hybridization among Cr, N, and the nearest-neighbor C in Cr$_{2V}$-N$_C$ configuration, which is favored under N-rich condition. The additional N changes little to the defect levels of Cr$_{2V}$ in the diamond gap, in favor of the optically active single photon emitters. Furthermore, it was found that the new defect levels would be coupled by thermal excitations as long as O is involved in the complex (with or without N), leading to a depletion of efficient SPSs.

II. METHODOLOGY

A. Computational details

Our first-principles calculations have been carried out with the spin polarized density functional theory (DFT) with the generalized gradient approximation (GGA) of PBE formulation for the exchange and correction functional. The electrons of $2s^22p^6$, $2s^22p^5$, $2s^22p^4$, $3d^4s^1$ were treated as valence for C, N, O, and Cr, respectively. A plane-wave basis set and the projector augmented wave potentials were
employed as implemented in the Vienna \textit{ab initio} simulation package (VASP). An energy cutoff of 500 eV was used throughout the calculations. In the single center calculations, a 64-atom ($2 \times 2 \times 2$) cubic supercell was employed and Brillouin zone (BZ) sampling was carried out by using gamma centered $6 \times 6 \times 6$ k-point mesh. The structures are relaxed until the Hellmann–Feynman forces are less than 0.01 eV/Å. Theoretically calculated equilibrium lattice parameter of diamond, $a = b = c = 3.573 \text{ Å}$, was employed, when the corresponding experimental value is 3.567 Å.

**B. Defect formation energy calculations**

In order to evaluate the energetic stability of these defects, we calculated the defect formation energy $\Delta H_f(x, q)$ as a function of the Fermi energy $\varepsilon_F$, as well as atomic chemical potentials $\mu_a$. 

$$\Delta H_f(x, q) = E(x, q) - E(\text{host}) - \sum_a n_a \mu_a + q(\varepsilon_F + E_V),$$

where $E(x, q)$ stands for the total energy of the super-cell with the corresponding defect at charge state of $q$, $\varepsilon_F$ is measured with respect to the valance band maximum (VBM) $E_V$ of the host material, $n_a$ is the number of elements that have been added to ($n_a > 0$) or removed from ($n_a < 0$) the super-cell. The chemical potential $\mu_a$ depends on the dynamic growth, here the chemical potential of $\mu_Cr$ is chosen under C-rich condition with a restriction of avoiding the formation of CrC, i.e.,

$$\mu_Cr = \mu_Cr^{\text{bulk}} + \Delta H_f(CrC).$$

The chemical potential of $\mu_C$ was taken from pure diamond. The defect transition energy level $\varepsilon_x(q/q')$ is the Fermi energy in Eq. (1) at which the formation energy $\Delta H_f(x, q)$ of defect $x$ and charge $q$ equals to that of another charge $q'$ of the same defect

$$\varepsilon_x(q/q') = \frac{\Delta H_f(x, q) - \Delta H_f(x, q')}{q - q'}.$$

For the image charge effect, the Makov-Payne correction up to the dipole term was adopted in this work. In fact, the transition levels changes within several meV when we employed a recent approach, which considered the potential alignment between the pure and defected systems. This implied that Makov-Payne correction up to the dipole term is reasonable for the transition level calculations.

### III. RESULTS AND DISCUSSION

#### A. Stability of Cr single defects in diamond

We considered three types of point defects for single Cr defects in a diamond, including tetrahedral interstitial Cr (Cr_{int}), Cr substituting for C atom (CrC), and Cr atom in the center of the carbon divacancy (Cr_{2V}), as depicted in Figure 1. We found that the tetrahedral interstitial Cr remains in all charge states, with nearest and the second nearest Cr_{int}-C bonds elongated by up to 8.93% and 12.25%, respectively. For the substitutional Cr, the Cr atom remains at the lattice site with a $T_d$ symmetry, where the Cr_{C}-C bonds are elongated by about 15.5% and 14.8% in the stable charge states of $0$ and $1^-$, respectively. Interestingly, the neutral Cr_{2V} undergoes a symmetry-breaking distortion to a configuration with Cs symmetry, as the two groups of Cr_{2V}-C bond lengths along the symmetry axis change by $-2.6\%$ and $10\%$, and the other two groups of nonequivalent bond lengths change by $-0.5\%$ and $10\%$, respectively. The Cr ion of Cr_{2V}, Cr_{2V}^2, and Cr_{2V}^- remain at the center of divacancy, keeping the D_{3d} symmetry with the Cr_{2V}-C bonds uniformly elongated by about $3\%$–$4\%$. The local structures of these optimized configurations are well consistent with previous work by Assali and Benecha and Lombardi.

The formation energies of three single Cr defects with various charge states are depicted in Figure 2. $\Delta H_f(x, q)$ depends on the Fermi level ($\varepsilon_F$), which is referenced to the VBM of the bulk host material. For each defect, only the charge state with the lowest $\Delta H_f(x, q)$ is shown at a given $\varepsilon_F$. From Figure 2, we found that Cr is energetically favored at the divacancy site in the charge states of $0$, $1^-$, $-2^-$, and $-3^-$ compared to CrC and Cr_{int} defects. This is in line with the recent theoretical results by Benecha and Lombardi and the experimental observations for other transition metals, such as Ni and Co, incorporated synthetic diamond during high pressure and high temperature growth.

The calculated stable charge states of Cr_{int}, CrC, and Cr_{2V} defects are ranged from $2^+$ to $1^-$, $0$ to $1^-$, and $0$ to $3^-$ (cf. Fig. 2), respectively. This is slightly different from the results of Assali \textit{et al.} (2\% to 1\%, 2\% to 2\%, and 0\% to 3\% for Cr_{int}, CrC, and Cr_{2V} defects) and Benenda \textit{et al.} (2\% to 2\% for CrC and 0\% to $-6$ for Cr_{2V}). The discrepancies should be ascribed to the different treatment on the transition levels, as no any corrections applied in Ref. 13 and only the VBM correction with partly image charge correction in Ref. 30. In our calculations, we adopted the dipole correction to the formation energies, and cross-checked with a recent approach suggested by Samuel \textit{et al.}.

#### B. Stability of (Cr, O), (Cr, N), and (Cr, N, O) in diamond

Before the investigation of Cr defect complexes with O and/or N, the local structure of Ni complexes with N in diamond has been studied intensively. It was regarded that the most possible defect complexes are two classes of NiN complexes: the low symmetry semi-vacancy N_{Ea} centers (a Ni atom in the center of a semi-vacancy with n C replaced with N) and the higher symmetry A_{Bc} centers (a substitutional nitrogen with n N neighbours). Possible (Ti, N) defect complexes made up of a substitutional Ti with an neighbor N and Ti in a double semi-vacancy with one neighboring N were also proposed. Based on experimental observations of Cr-related defects, Aharonovich \textit{et al.} proposed that the possible Cr-related defect complexes could be a Cr-X or X-Cr-Y type non-centrosymmetric atomic configuration, where X and Y are likely to be oxygen (sulphur), nitrogen, or vacancy.

Here, we considered two possible configurations of (Cr, O) and (Cr, N) defect complexes, as well as two possible...
configurations of (Cr, N, O), namely CrC-O, Cr2V-O, CrC-N, Cr2V-N, Cr2V-N-(f)O, and Cr2V-N-(s)O, as shown in Figure 1. CrC-O stands for a nearest-neighboring substitutional Cr-O pair, while Cr2V-O refers to a Cr2V with an adjacent substitutional oxygen. Correspondingly, CrC-N and Cr2V-N are also considered in analogy for the Cr defect complexes involved with N. Two possible complexes of Cr involved with both N and O considered are: a Cr2V-N center with a first neighbor substitutional oxygen, Cr2V-N-(f)O, and a Cr2V-N center with a second neighbor.

FIG. 1. The optimized local structures of the defects Crint, CrC, CrC, Cr2V, CrC-O, Cr2V-O, CrC-N, Cr2V-N, Cr2V-N-(f)O, and Cr2V-N-(s)O in diamond (only structures of their neutral charge states are shown here). The related bond lengths and corresponding symmetry are also given in the figure.
substitutional oxygen Cr2V-NC-(s)OC. Additionally, the configurations of Cr2V-\(n\)OC and Cr2V-\(n\)NC (\(n = 2, 3, 4, 5, 6\)) are also studied in analogy to the NE\(n\) nickel nitrogen complexes.\(^3\) The defect pair of CrC with a second nearest-neighboring substitutional O or N is not considered here since their formation energies are about 1.5 eV higher than that of CrC-OC and CrC-NC correspondingly in a test calculation. Meanwhile, defect pairs of Cr2V with a second nearest-neighboring OC and NC are also not considered since their formation energies are 2.90 eV and 1.54 eV higher than that of Cr2V-OC and Cr2V-NC, respectively, suggesting a tendency for the formation of defect complexes. Cr2V-NC-(s)OC center is studied here to have a deeper look of possible oxygen effect though its formation energy is 2.66 eV higher than that of Cr2V-NC-(f)OC center.

Structural optimizations indicate that CrC-OC and CrC-NC undergo outward relaxations to a C\(_3\)V symmetry in all the charge states. Both Cr2V-OC and Cr2V-NC centers undergo outward relaxations with symmetry breaking distortions, yielding these two centers to a C\(_S\) symmetry, with a single-mirror plane operation. This is in line with the experiment suggestion that the center has a non-centrosymmetric atomic configuration.\(^1\) Under O-rich and N-rich conditions, the Cr2V-NC-(f)OC center, with a C\(_1\) symmetry, has a formation energy of 7.55 eV, higher than that of Cr2V-NC center at the neutral charge state. From Figure 3, we can see that Cr2V-OC and Cr2V-NC centers are also more stable than CrC-OC and CrC-NC at all the charge states, respectively.

In order to investigate the stability of the defect complex in various doping concentrations of oxygen and nitrogen, we also considered the configurations of Cr2V-nOC and Cr2V-nNC (\(n = 2, 3, 4, 5, 6\)), namely, with two to six adjacent substitutional oxygen or nitrogen connecting with Cr atom. The possible configurations and the formation energy of these neutral defects are summarized in Table I. We also calculated the formation energy of Cr2V-nO\(_C\) centers at various

### Table I
<table>
<thead>
<tr>
<th>Center</th>
<th>Symmetry</th>
<th>Spin</th>
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<tr>
<td>Cr2V-6NC</td>
<td>D(_3d)</td>
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</table>

FIG. 2. Formation energies of single doped Cr defects (Cr\(_{\text{ant.}}\), CrC, and Cr2V represented by black, blue, and red, respectively) at various charge states in diamond as a function of the Fermi level.

FIG. 3. Formation energies of co-doped Cr defects (Cr\(_{\text{ant.}},\) CrC, and Cr2V represented by black, blue, and red, respectively) at various charge states in diamond as a function of the Fermi level. Here, the chemical potentials of N and O are assumed at N-rich and O-rich condition, respectively.

FIG. 4. The formation energy of (Cr2V-nO\(_C\)) complexes (\(n = 1–6\)) under various oxygen chemical potentials, with corresponding temperature of O\(_2\) at 1 atm shown at the top.
FIG. 5. Band structures of pure diamond (a), CrC (b), Cr₂V (c), Cr₂V-NC (d), Cr₂V-OC (e), Cr₂V-NC-(f)OC (f), obtained from 64-atom supercell calculations. Blue and red (dotted) lines represent spin up and down bands, respectively. Fermi energy (VBM for the pure system) is set to zero, and all the band structures of the defects are corresponding to their neutral charge state.

FIG. 6. Energy-level diagram for divacancy Cr impurity in diamond, Cr₂V. Left and right panels show how majority (↑) and minority (↓) levels arise from hybridization of Cr atomic states with diamond divacancy states.
charge states with respect to the chemical potentials of oxygen with the Fermi level chosen at VBM since diamond is a p-type semiconductor intrinsically. Figure 4 shows the formation energy of \((\text{Cr}_{2V}-n\text{O}_C)\) complexes \((n = 1–6)\) under various oxygen chemical potentials. The corresponding data of temperature and pressure with respect to the chemical potential of oxygen are taken from the work done by Reuter and Scheffler. From Table 1 and Figure 4, we can see that the formation energy of \(\text{Cr}_{2V}-n\text{O}_C\) increases as the number of neighboring O ions \((n)\) increases even under oxygen-rich condition. This indicates that \(\text{Cr}_{2V}-n\text{O}_C\) centers with multiple neighboring oxygen ions are unlikely to form even under high concentration of oxygen due to relatively high formation energies. The \(\text{Cr}_{2V}-n\text{N}_C\) complexes are also unstable as \(\text{Cr}_{2V}-n\text{O}_C\) centers. According to our calculations, the most stable co-doped \(\text{Cr}_{2V}-n\text{O}_C\) and \(\text{Cr}_{2V}-n\text{N}_C\) configurations are found to be \(\text{Cr}_{2V}-\text{O}_C\) and \(\text{Cr}_{2V}-\text{N}_C\) center, respectively. From Figure 3, we see that \(\text{Cr}_{2V}-\text{O}_C\) center is energetically most stable in the charge states of \(+1, 0, -1, -2,\) and \(\text{Cr}_{2V}-\text{N}_C\) of \(0, -1, -2.\)

C. Electronic structures of the defect complexes

Figure 5 shows the band structures of neutral \(\text{Cr}_{C}, \text{Cr}_{2V}, \text{Cr}_{2V}-\text{N}_C, \text{Cr}_{2V}-\text{O}_C, \text{Cr}_{2V}-\text{N}_C-(f)\text{O}_C\) along with that of pure diamond for comparison. The calculated band gap for pure diamond \((E_g = 4.2 \text{ eV})\) is in good agreement with earlier theoretical results. It is found that the single incorporation of Cr or co-incorporation of Cr and N into diamond carbon divacancy induces strongly spin-polarized impurity levels in the diamond band gap, while the semiconducting property of diamond is conserved in both spin channels. Based on the crystal-field theory, the electronic states of \(\text{Cr}_{2V}\) can be well interpreted as a result from an interaction between the
divacancy states and those of the Cr atom. The removal of two carbon atoms from the diamond lattice leads to a defect with $D_{3d}$ symmetry, as depicted in Figure 6. The one-electron ground-state structure of a diamond divacancy in $D_{3d}$ symmetry has the $a_{2g}^2a_1g^2e_u^0$ configuration, which is similar to the situation of manganese in a diamond divacancy. Consequently, the Cr 3d energy levels split into $2e_g + a_{1g}$. When a Cr atom is placed in the middle position of a divacancy, its $e_g$ energy level interacts with the carbon dangling bonds, leaving a fully occupied nonbonding $t_{2g}$-like $(e_g + a_{1g})$ orbital inside the valence band. On the other hand, the $e_g$ state of Cr interacts with the divacancy $e_g$ gap level, leaving the $e_g$-bonding level in the valence band and the $e_g$-antibonding one unoccupied in the band gap. Based on our calculation, the symmetry of Cr$_2$V lowers from $D_{3d}$ to $C_5$ as a result of the Jahn–Teller effect, which leads the degenerate $e_g$ state into single states. When NC is coupled with the Cr$_2$V defect, the calculated band structure of Cr$_2$V-NC, as shown in Figure 5, keeps the characteristics of Cr$_2$V: two majority spin defect levels and three minority spin defect levels in the band gap with the relative positions analogy to that of Cr$_2$V. The main difference is that the calculated band gap of diamond with Cr$_2$V-NC is about 1 eV smaller than that of Cr$_2$V. Figure 7 illustrates the total and partial density of states of single doped and co-doped defects of the neutral charge state. For Cr at a divacancy, it is clear to see that these impurity bands originate from $s$, $p$-$d$ hybridization between carbon $2s$, $2p$, and Cr 3d orbitals. This scenario also applies to the Cr$_2$V-NC center. While for Cr$_2$V-OC center, there is no strong orbital hybridization among carbon, oxygen, and chromium atoms, leading to many not-well-separated impurity levels in the band gap. This is not sufficient to form optical centers of narrow emission line since electrons could be transited thermodynamically between the defect levels. Similar to the Cr$_2$V-OC center, the band structure of Cr$_2$V-NC-(f)-OC center also has many closely distributed impurity levels in the band gap.

Based on the formation energies and the electronic properties, we suggested that Cr$_2$V-NC center should be responsible to the recent reported Cr-related bright single-photon emitter centers in diamond when N is involved. Nevertheless, we found that all the oxygen involved Cr defect would introduce many closely distributed impurity levels in the band gap and would degrade the property of Cr-related SPS. This might be not in line with the experimental report that proper O concentration would improve the performance of Cr-related SPS in diamond, and further computational and experimental researches are suggested to clarify the discrepancy.

IV. SUMMARY

In summary, we have investigated the stability and electronic structure of various O and (or) N coupled Cr defects in diamond. Our calculations showed that the Cr$_2$V-NC center has a $C_5$ symmetry, and introduces strongly spin polarized impurity levels into the diamond band, in favor of SPS as Cr$_2$V centers. We suggested that the recently observed chromium-related bright single photon emitter in diamond may be Cr$_2$V or Cr$_2$V-NC centers. Under N-rich condition, the low formation energy of Cr$_2$V-NC center can improve the concentration of SPS. The additional incorporated O will form complexes with Cr$_2$V or Cr$_2$V-NC defects, and introduces many not-well-separated impurity levels. This would significantly broaden the emission line and thus degrades the quality of Cr$_2$V or Cr$_2$V-NC as SPS.

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